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REPORT
ON THE
QUANTUM THEORY OF SPECTRA

BY
L. SILBERSTEIN, Ph.D.

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L. SILBERSTEIN, PH.D.

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PREFACE

THE present report was written originally for the private use of Messrs. Adam Hilger, and was then, at their instance, amplified and prepared for publication. But even with this extension it will be found to contain a brief account of only the most important contributions to the Quantum Theory of Spectra, a new field of inquiry opened only six or seven years ago by Niels Bohr, but already very vast and rapidly growing and ramifying in multiple directions. It will, no doubt, soon call for a supplement. As it is, however, it is hoped to be a helpful guide for those desiring to enter upon this new and strangely fascinating line of thought and investigation.

I take the opportunity of expressing my best thanks to Messrs. Hilger for bringing me into closer contact with this refreshing new line of thought of the modern spectroscopists. My thanks are also due to my beloved teacher, Prof. Max Planck, and to my friend, Prof. A. W. Porter, for reading the proof slips, and to Messrs. MacLehose for the indefatigable care they have bestowed upon this book.

L. S.

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REPORT ON THE QUANTUM THEORY OF SPECTRA.

1. The present report, which I shall attempt to bring up to date, is based upon the reading and scrutiny of the following original papers :

1. N. Bohr, *Phil. Mag.*, xxvi, pp. 1-25, 1913.
2. ,, ,, xxvi, 476-502, 1913.
3. ,, ,, xxvi, 857-875, 1913.
4. ,, ,, xxvii, 506-524, 1913.
4*a*. ,, ,, xxix, 332-335, 1915.
5. Th. Wereide, *Annalen der Physik*, xlix, 966-1000, 1916.
5*a*. ,, *ibid.*, lii, 276-290, 1917 (three notes).
6. M. Planck, *ibid.*, l, 385-418, 1916.
7. P. S. Epstein, *ibid.*, 489-520, 1916.
8. ,, ,, 815-840, 1916.
9. F. Paschen, *ibid.*, 901-940, 1916.
10. A. Sommerfeld, *Ann. d. Physik*, li, 1-94, 1916.
11. ,, ,, ,, ,, 125-167, 1916.
11*a*. K. Glitscher, *ibid.*, lii, 608-630, 1917.
12. P. S. Epstein, *ibid.*, li, 168-188, 1916.
13. K. F. Herzfeld, *ibid.*, 261-284, 1916.
14. P. Ehrenfest, *ibid.*, 327-352, 1916.
15. N. Bohr, *Danisk Acad. Sc.*, IV, 1, Parts I and II, pp. 1-100, 1918.
16. M. Planck, *Annalen der Physik*, lii, pp. 491-505, and liii, pp. 241-256, 1917.
17. J. M. Burgers, *ibid.*, pp. 195-202, 1917.
18. H. A. Kramers, *Mémoires Acad. Sc., Copenhagen*, 8th ser., iii, No. 3, pp. 287-384, 1919.
19. L. Silberstein, *Phil. Mag.*, xxxix, January 1920.

These papers will, whenever the need occurs, be referred to by the attached numbers [in square brackets]. In addition to this

first-hand material may be mentioned Mr. J. H. Jeans' *Report on Radiation and the Quantum Theory*, Physical Society of London, 1914 (pp. iv + 90), in which a few pages (pp. 50-57) are dedicated to Bohr's elementary theory of line spectra. Jeans' *Report* may be recommended for a rapid and easy initiation into Planck's theory of quanta in connection with black-body radiation, the knowledge of which I here presuppose, at least as far as its rudiments are concerned. With regard to the nucleus structure of the atoms (upon which all these spectrum theories are based) and to the experimental evidence for such a structure, it is advisable to consult Rutherford's papers, which are easily accessible (*Phil. Mag.**) and as easily read. There is no need for incorporating here a description of Rutherford's work.

2. The strong side of the quantum theory of spectra, as first proposed by Bohr [1] and further developed by Sommerfeld and others, consists in its very remarkable agreement with experiment, which in certain directions can be traced even to minute details of observations, such as the fine-structure of the 'lines' or groups of Fowler's helium series; the weak side of the theory consists in the heavy sacrifices it requires at the very outset, *e.g.* the abandonment of otherwise well-established principles of mechanics and of electromagnetism, in addition to the radical innovation inherent in the discontinuity of the very concept of Planck's quantum (quantum of 'action,' that is, 'Wirkungsquantum'), which is one of the most essential parts of the spectrum theory under consideration. The agreement, however, is of such a startling nature that the theory deserves, in spite of all these heavy sacrifices, and notwithstanding its somewhat magically arithmetical character, the greatest active interest of the modern physicist. Moreover, some of the recent predictions of the new theory require, for their experimental verification, a further refinement of spectroscopic apparatus and methods of observation, which soon may find an echo in the optician's workshop.

The best way to become acquainted with the fundamental assumptions and with the chief results of the quantum theory of spectra will be to consider, in some detail, the simplest atomic

* The chief of these papers is published in vol. xxi of *Phil. Mag.* (1911), p. 669.

system, to wit, the hydrogen atom, which—according to Rutherford and his school—consists of a single electron (of mass m and charge $-e$) circling round a single positive *nucleus*, *i.e.* an electric positive charge $(+e)$ contained in such a small volume that it represents almost entirely the mass of the hydrogen atom.*

In Bohr's first attempt at a spectrum theory [1, also 2, 3], the electrodynamic as well as the relativistic complications of the motion are disregarded, and only the purely electrostatic attraction between the nucleus and the electron is taken into account. In short, the motion is treated as ordinary Keplerian planetary motion (inverse square law), well-known since the beginnings of Celestial Mechanics. Moreover, to begin with, the mass of the nucleus is treated as infinite, in comparison with that of the planet or the electron, so that the vector equation of motion of the electron is simply

$$\ddot{\mathbf{r}} = -\frac{e^2}{mr^2}\mathbf{u}, \tag{1}$$

e being the charge in ordinary or so-called 'irrational,' electrostatic units, and $\mathbf{r}=r\mathbf{u}$, the vector drawn from the nucleus to the electron. It is scarcely necessary to say that writing down (1) as the equation of motion, the force-component corresponding to electromagnetic radiation is disregarded,—as already stated. But it is of importance to note that radiation is thus 'disregarded' not simply as a means of getting a first approximation, but it is disregarded radically, with purpose; it is *suspended*, in virtue of a postulate of the theory, precisely for the whole duration of validity of this smooth, Newtonian motion. In other words, apart from the small corrections due to relativity and due to the finite mass of the nucleus, the above equation (1) is assumed to hold *rigorously*, and the electron is assumed *not to radiate at all while it describes round the nucleus any of the Keplerian orbits* contained in (1).

And herein lies the chief of the sacrifices: the validity of Maxwellian principles is denied to these electronic orbits; notwithstanding that the motion of the electron is not uniform, it does not

* It will be kept in mind that 'mass' stands here for electromagnetic mass, and this is inversely proportional to the radius of the, say, spherical charge. Thus, according to Rutherford, the linear dimensions of the hydrogen nucleus would be about 1840 times smaller than those of an electron, and, therefore, of the order of 10^{-16} cm.

radiate any electromagnetic energy while describing any of these orbits.*

Excluding hyperbolic and parabolic orbits (since we are not interested here in electrons which are abandoning their atoms), the orbits corresponding to (1) are *ellipses* described by the electron according to the ordinary laws of Kepler. Thus, if $2a$ be the major axis of such an ellipse, and T the period of revolution, we have the well-known relations [with v = velocity at any instant]

$$\frac{1}{a} = \frac{2}{r} - \frac{mv^2}{e^2}; \quad \frac{T^2}{a^3} = \frac{4\pi^2 m}{e^2}, \tag{2'}$$

whence, denoting the negatived total energy of the system, $\frac{e^2}{r} - \frac{1}{2}mv^2$, by W,

$$2a = \frac{e^2}{W}; \quad \frac{1}{T} = \frac{\sqrt{2}}{\pi} \frac{W^{\frac{3}{2}}}{e^2\sqrt{m}}, \tag{2}$$

giving the major axis and the frequency of revolution $\frac{1}{T}$ in terms of the negatived total energy W, which, of course, remains constant during the Keplerian motion in question.

Now comes Bohr's further assumption, which is not less revolutionary than the suspension of radiation already mentioned. It is most important to make this assumption as plain as is possible:

If the nucleus were our Sun and the electron a planet, say our Earth, the latter could—under given 'initial' conditions—describe any one of the multiply-infinite class of Keplerian orbits given above, and each of these would be stationary and, as such, possible for the planetary system for ever.

Now, according to Bohr's assumption, *only certain of these Keplerian orbits and motions are possible as 'stationary'* states of motion of the atomic system (hydrogen atom = nucleus and electron), viz. in each plane through the nucleus a certain *discrete* series of Keplerian motions, corresponding to a *discontinuous series of values of the angular momentum* and, therefore, of the energy constant W, appearing in (2).

* Th. Wereide's attempt to replace the usual radiation formula by a slightly different one which would give no radiation for uniformly described circular orbits [5*a*, first note] does not change very much the state of things. Nor is Prof. Wereide's reasoning, leading to the new radiation formula, free from serious objections.

The procedure of picking out or ' quantizing ' [Sommerfeld says : ' quanteln '] these privileged values and the corresponding Keplerian motions is based upon Planck's universal constant h, the ' Wirkungsquantum,' which appears in his famous formula for the black-body radiation.* The principle of such quantizing has undergone of late several subtle modifications (or, in part, generalizations), of which we will speak later on. To begin with, however, it will be best to give the principle as it appears in Bohr's first paper [1]. Bohr limits himself here to the consideration of *circular* orbits, and then the principle in question is equivalent to the following assumption :

Stationary states of motion are those and only those for which *the angular momentum* of the electron is equal *to an exact multiple of an universal constant*, to wit, of $h/2\pi$, *i.e.*

$$2\pi \times \text{angular momentum} = nh, \tag{3}$$

where n is an integer.

This is, in Bohr's case under consideration, equivalent to putting, for the ' stationary ' states,

$$W = W_n = \frac{nh}{2T}. \tag{3a}$$

By (3*a*) and (2) we have

$$W = W_n = \frac{2\pi^2 me^4}{h^2} \cdot \frac{1}{n^2}, \tag{4}$$

and

$$a = a_n = \frac{h^2 \cdot n^2}{4\pi^2 \cdot me^2}. \tag{5}$$

At this stage it may be well to note, parenthetically, that if q be the angle between the variable radius vector and a fixed radius vector, the kinetic energy for circular orbits is

$$\mathrm{T} = \tfrac{1}{2} m\dot{q}^2 r^2,$$

and the moment p (in Hamilton's sense of the word) corresponding to the configurational coordinate q is

$$p = \frac{\partial \mathrm{T}}{\partial \dot{q}} = mr^2\dot{q} = \text{angular momentum}.$$

* It will be recalled that, according to Planck's theory, radiation from an atomic system takes place in quanta (separate emissions), the energy radiated out by an oscillator of frequency ν in each single emission being equal to $n \cdot h\nu$, where n is an *integer*. Planck's constant equals about $6{\cdot}5 \cdot 10^{-27}$ C.G.S. Dimensions : $[h] = [\text{energy} \times \text{time}] = [ml^2t^{-1}] = [\text{angular momentum}]$.

Thus the quantizing principle (3) can be written

$$2\pi p = nh,$$

and since p is constant (Kepler's second law), this is the same as

$$\int_0^{2\pi} p\, dq = nh, \tag{3b}$$

or, in words: $p\,dq$ integrated *over a full period* of the motion is equal *to an exact multiple of h*. It is precisely this form which has turned out more recently to be adaptable to cases more general than that treated by Bohr in his first essay.

Thus, out of all circular orbits only such whose radii are given by (5) are 'stationary'.* Imagine, now, a series of such stationary orbits, No. 1, 2, 3, etc., to which correspond the energy constants W_1, W_2, W_3, etc., given by (4), with $n = 1, 2, 3$, etc. As long as the atom is left to itself, the electron will move along one of these (and these *only*) without ever emitting any radiation. [Maxwellianism suspended, ordinary mechanics fully valid.] But if through some foreign agency whose mechanism cannot yet be treated mathematically the *electron is thrown out from its stationary orbit* (n) *to another stationary orbit* (n'), *it suddenly radiates out the difference of energies* in the *form of monochromatic waves*, of a frequency ν, say, and Bohr's new assumption is precisely this:

$E_n = -W_n$ being the total energy on the initial, and $E_{n'} = -W_{n'}$, that on the final stationary orbit, *the emitted frequency* ν *is such that*

$$E_n - E_{n'} = \nu h,$$

i.e.

$$W_{n'} - W_n = \nu h. \tag{6}$$

Needless to say the founder of the new theory and his followers do not attempt to describe the mechanism of such an extraordinary performance, one, that is, that enables the atomic system to hit precisely upon the frequency ν required by the assumption (6). [But future generations may be able to reduce this assumption to something more plausible and more familiar,—when it will cease to be a mere assumption. After all, (6), is not more and not less extravagant than what Planck requires for his black-body radiation.]

* Notice that the smallest of these quantized radii is, by (5), $a_1 = \frac{h^2}{4\pi^2 m e^2}$, which is about $0{\cdot}6 \cdot 10^{-8}$ cm., *i.e.* of the atomic order.

The last assumption, as well as the preceding ones, being granted, introduce into (6) the values of W_n, $W_{n'}$ from (4). Then the result will be, the corresponding *spectrum series*,

$$\nu = \frac{2\pi^2 me^4}{h^3}\left[\frac{1}{n'^2} - \frac{1}{n^2}\right], \tag{7'}$$

where n', n are integers. This is one of Bohr's most elegant results. Putting $n' = \text{const.}$ and letting n assume a series of integral values ($n > n'$), we have in (7') a series of spectrum lines, *converging* towards $\nu_{n=\infty}$ as the '*head*' of the series.

In (7') ν is the reciprocal of the period of the emitted waves; in experimental work it is usual to quote the reciprocal $1/\lambda$ of the wave-length in vacuo. Since this is $= \nu/c$, we have, ultimately,

$$\frac{1}{\lambda} = N\left[\frac{1}{n'^2} - \frac{1}{n^2}\right], \tag{7}$$

where

$$N = \frac{2\pi^2 me^4}{ch^3}, \tag{8}$$

c being the light velocity in vacuo. If we take $n' = \text{const.} = 2$, we have in (7) the well-known Balmer series of hydrogen ($n = 3, 4, 5, \ldots$); $n' = \text{const.} = 3$ gives the infra-red series predicted by Ritz and observed by Paschen.

A further, very remarkable result of Bohr's elementary theory is that the factor N in (7), as defined by (8), is not only of the order of Rydberg's well-known constant, $N_R = 109675$ cm.$^{-1}$, but coincides with it numerically pretty well when the values of the electronic constants e, m and that of h (derived from experiments on black-body radiation, and from other sources) are substituted. In fact, with

$$e = 4{\cdot}7 \cdot 10^{-10}; \quad \frac{e}{m} = 5{\cdot}3 \cdot 10^{17} \,(i.e.\ m = 0{\cdot}9 \cdot 10^{-27});$$

$$h = 6{\cdot}5 \cdot 10^{-27}; \quad c = 3 \cdot 10^{10}$$

(everything in c.g.s.), formula (8) gives

$$N \doteqdot 1{\cdot}005 \cdot 10^5,$$

differing from Rydberg's constant only by 9 per cent., which is well within the limits of error of m, e^4, h^3. This coincidence seems to be a very strong support of the theory.

Notice that (7), (8) do not contain any new empirical constants.

3. For spectroscopic purposes, of course, the 5 or 6-figure value of N will not be calculated from the very uncertain values of e, m, h, but from the observed lines of the spectrum in question (here that of hydrogen). It is well known that $N = 109675$ represented excellently (with $n' = 2$; $n = 3, 4, 5$, etc.) Balmer's series or the so-called diffuse series of hydrogen. For other elements (notably for helium) the factor N is slightly different. But, and this is again a very remarkable result, even these slight differences can be accounted for by taking into consideration the *finite* mass (say, M) of the nucleus in question. In fact, this converts m in (8) into

$$\frac{mM}{M+m},$$

so that the quantum value of the Rydberg factor becomes slightly smaller, viz., instead of N,

$$N' = \frac{M}{M+m} N. \qquad (8')$$

A very elegant application of this correction-factor has been made by Fowler, and later by Paschen. It will be mentioned presently.

4. The *details* of the quantum theory of spectra for atoms whose nuclei carry the charge $2e$ (as helium) or $3e$, etc., are up to the present not quite satisfactory. But even in the present crude state the theory as applied to helium has yielded some very interesting results.

According to Rutherford's well-supported opinion the atom of helium consists of a nucleus whose charge is $2e$ and, therefore, in its neutral state, there must be *two* electrons circling round the nucleus. Thus $e^2 = e \cdot e$ in the equation of motion (1), p. 3, is now to be replaced by

$$e \cdot 2e = 2e^2.$$

If the perturbations of the motion of one of the electrons due to the other electron are simply neglected,* or better, if the helium

* As in Bohr's first paper [1, p. 10]. The neglect of such perturbations does not seem satisfactory. Equally unsatisfactory is Bohr's later assumption [2, p. 477], that the electrons of more complicated atomic systems 'are arranged at equal angular intervals in coaxial rings,' and that a whole ring of electrons jumps simultaneously from one stationary state of motion to another. It is scarcely necessary to point out the unlikelihood of such configurations and processes. The assumptions of Bohr's [2] lead him again to the same result (9); cf. [2, p. 488].

atom in question is *ionized* and thus retains only one of its electrons, everything will be as before, except that e^4 in (8) will be replaced by

$$(2e^2)^2 = 4e^4,$$

i.e., still disregarding the finite mass of the nucleus, N will be replaced by $4N$, so that, instead of (7) we shall have,

$$\frac{1}{\lambda} = N\left[\frac{1}{(n'/2)^2} - \frac{1}{(n/2)^2}\right]. \qquad (9)$$

Now, if we put here $n' = 3 = \text{const.}$, and $n = 4, 6, 8$, etc., or $n = 5, 7, 9$, etc., we get Fowler's 'first' and 'second principal' series of helium, respectively (cf. *M. N. of R. A. S.*, vol. 73, Dec. 1912, p. 62 *et seq.*), which properly constitute but *one* series. [Notice in passing that $n' = \text{const.} = 4$ gives the series observed by Pickering in the spectrum of the star ζ Puppis.]

Now, Fowler's measurements are tolerably well represented when we take in (9),

(*a*) $$\tfrac{4}{9}N \equiv \tfrac{4}{9}N_{He} = 48764{\cdot}0,$$

while $\frac{4}{9}$ of 109675 (hydrogen) is

(*b*) $$\tfrac{4}{9}N_H = 48744{\cdot}4.$$

According to (8′) we should have

(*c*) $$\frac{N_{He}}{N_H} = \frac{1 + m/M}{1 + \frac{1}{4}m/M},$$

where m/M is the ratio of the mass of the electron to that of the hydrogen atom (remember that the atomic weight of He is four times that of H). Now, on substituting in the right-hand member of (*c*) the numbers (*a*), (*b*), we get

$$\frac{m}{M} = 1 : 1836,$$

which is in excellent agreement with other determinations of the mass ratio of the electron and the hydrogen atom. This is the remarkable result hinted at before: a refinement of the theory due to taking into account the finite mass of the central body of the atomic system.

5. A further refinement, which is due to Sommerfeld [10], consisted in taking account of the *relativistic* complications of the original Keplerian motion of the electron. This refinement, which yielded the fine-structure of spectrum lines, will now occupy our

attention, together with the generalization of Bohr's original quantizing principle, made by Sommerfeld himself, on the lines laid down by Planck, Ehrenfest, and others.

Since bi- and poly-electronic atomic systems are not yet worked out satisfactorily, it will be best to speak henceforth exclusively of *the single-e* nucleus with its *single* electron, as in the hydrogen atom.* Such, in fact, is the case of Sommerfeld, paper [10], and also of Epstein's investigations concerning the Stark effect,—to be treated in a subsequent section.

Sommerfeld's investigations, more especially [10], deserve careful attention, and will, therefore, be treated here at some length.

It will be remembered that Bohr, in his first papers (1913-14), limited himself to the consideration of circular orbits. But, as Sommerfeld justly remarks, the electron cannot be prevented from choosing an elliptic orbit, and he shows that—contrary to Bohr's original statement—this is by no means irrelevant for the final result. In fact, if the angular momentum alone is quantized, the result would be a series of diffuse bands, not sharp lines (as will be shown presently). In short, in Bohr's treatment the atomic system (hydrogen) appeared as a system with one degree of freedom, while —admitting ellipses of every eccentricity, and still confining himself to a plane—Sommerfeld treats it more completely, that is, as a system of two degrees of freedom.

Let q_1, q_2 be the two configurational coordinates, say the polar coordinates ϕ, r of the electron, T the kinetic energy as function of the q and $\dot{q}$, $p_1=\frac{\partial T}{\partial \dot{q}_1}$, $p_2=\frac{\partial T}{\partial \dot{q}_2}$, the corresponding moments. More especially let q_1, q_2 be *canonical* coordinates [such are precisely the said r, ϕ], that is, in which, the equations of motion assume the well-known Hamiltonian canonical form. Then, basing himself in part on Planck's investigations [6] and in part upon his own modifications of Planck's reasoning (cf. also [12] and [14]), Sommerfeld adopts as a quantizing principle, for each of the q's, and for the case of two or of any number of degrees of freedom,

$$\int p_i\, dq_i = n_i h, \tag{10}$$

* The reasoning, with N replaced by $4N$, will apply also to *ionized* (not to neutral) He-atoms, such, that is, as have been deprived of one of their two electrons and retain but a single electron.

where n_i are positive integers, independently chosen for each degree of freedom, and h, as before, Planck's constant. He states himself explicitly that he has no support ('Berechtigung') for this 'Quantenansatz' or for the elementary, differential quantum cells which are equivalent to (10). As to the integration limits to be adopted in each of the equations (10) nothing very definite can be said *in general.* But when the motion, as in the present case [without relativity], is strictly periodic, he integrates $p\,dq$ over a full period, *i.e.* over $q_1=\phi$ from 0 to 2π, and over $q_2=r$ from $r_{\min.}$ (perihelion) to $r_{\max.}$ (aphelion) and back again,—or, which is the same thing, $\left(\text{writing } dr=\frac{dr}{d\phi}\cdot d\phi\right)$ over ϕ again from 0 to 2π. When the relativistic complications are taken into account the motion is no longer strictly periodic. Yet for moderate velocities (v/c = small fraction) the electron can be considered as describing a Keplerian ellipse with slowly moving perihelion [= peri-nucleon], and Sommerfeld says, therefore [10, p. 8], that 'the statistical manifold of the orbits is also here determined by a direction varying from 0 to 2π, as for instance that of the initial line of apses, so that here also the integration domain in ϕ is 2π, and does not depend on the shape of the orbit.' In short, without being able to support the procedure adopted, he applies it both without and with the relativistic complications. Properly speaking, its only support is a *post facto* one, to wit, the admirable agreement of the final results, especially those concerning the fine-structure of helium lines, with the experimental observations.

Sommerfeld treats first the atomic system without the relativistic terms. The motion is then strictly Keplerian. One first integral is the well-known $p_1=mr^2\dot{\phi}=$ const., and the equation of the elliptical orbit is

$$\frac{1}{r}=\frac{me^2}{p_1^2}(1+\epsilon\cos\phi), \tag{11}$$

where ϵ is the eccentricity. The total energy ($E=-W$) is easily found to be

$$E=-\frac{me^4}{2p_1^2}(1-\epsilon^2). \tag{12}$$

Now, if we were to quantize with respect to q_1 only, *i.e.* to make, by (10),

$$n_1 h = \int p_1 dq_1 = \int_0^{2\pi} p_1 d\phi = p_1 \int_0^{2\pi} d\phi = 2\pi p_1, \quad \text{or} \quad p_1 = \frac{n_1 h}{2\pi},$$

we should have, by (12), and by (6)—which Sommerfeld takes over from Bohr's theory without modification,—the spectrum series

$$\frac{1}{\lambda} = N\left(\frac{1-\epsilon_{n_1'}^2}{n_1'^2} - \frac{1-\epsilon_{n_1}^2}{n_1^2}\right), \tag{13}$$

where the eccentricities ϵ_n, $\epsilon_{n'}$ can assume all possible values. Thus we should have *no discrete series of sharp lines but* '*ein verwaschenes Band*,' to use Sommerfeld's own expression. To remedy this, Sommerfeld quantizes also with respect to the second variable (r), and through this he quantizes the *eccentricity*, which converts (13) into a series of sharp lines.

In fact, the moment p_2 or p_r is $\frac{\partial T}{\partial \dot{r}} = m\dot{r}$, and thus, by (10),

$$n_2 h = \int p_2 dr = m\int \dot{r}\, dr = m\int_0^{2\pi} \dot{r}\,\frac{dr}{d\phi}\, d\phi,$$

where n_2 is another positive integer, independent of n_1. Now,

$$\dot{r} = \frac{e^2}{p_1}\epsilon \sin\phi \quad \text{and} \quad dr/d\phi = \frac{p_1^2 \epsilon}{me^2}\,\frac{\sin\phi}{(1+\epsilon\cos\phi)^2},$$

in virtue of (11), so that

$$n_2 h = p_1 \epsilon^2 \int_0^{2\pi} \frac{\sin^2\phi}{(1+\epsilon\cos\phi)^2}\, d\phi = 2\pi p_1 \left(\frac{1}{\sqrt{1-\epsilon^2}} - 1\right),$$

whence, with $2\pi p_1 = n_1 h$ (as before),

$$1 - \epsilon^2 = \frac{n_1^2}{(n_1+n_2)^2}, \tag{14}$$

the required quantizing of eccentricity. Not only the angular momentum, but also the eccentricity of the 'stationary' orbits can have only certain values, to wit, those prescribed by (14), with $\frac{n_1}{n_2} = 1, 2, 3, \ldots$. This sounds strange; but by no means more strange than $2\pi p_1 = n_1 h$.

Now, substituting (14) into (13), the terms n_1^2 cancel out,* and the

* Here Sommerfeld becomes mystical; for in the circumstance that 'n_1^2 hat sich gerade herausgehoben,' so that n_1+n_2 only remains, he sees something particularly profound, and exclaims [10, p. 20]: 'Es scheint ausgeschlossen, dass ein so präzises und folgenreiches Ergebnis einem algebraischen Zufall (!) zuzuschreiben sein könnte.'

result is, with N as in (8), and with n_1', n_2' characterizing the final, and n_1, n_2 the initial orbit of the electron,

$$\frac{1}{\lambda} = N\left\{\frac{1}{(n_1'+n_2')^2} - \frac{1}{(n_1+n_2)^2}\right\}, \tag{15}$$

i.e. again the *Balmer series* of hydrogen, consisting of *sharp* lines, depending on *four* integers, 'die sich aber beim Wasserstoff sozusagen zufällig auf zwei ganze Zahlen $[n_1+n_2,\ n_1'+n_2']$ reduzieren.' In short, *the Balmer series of lines reappears completely*, but 'in ausserordentlich *vervielfachter Mannigfaltigkeit ihrer Erzeugungsmöglichkeiten.*' For now the total integer n_1+n_2 can be obtained in a variety of ways. In other words, to each possible value of the energy, which is given by

$$W = -E = \frac{cNh}{(n_1+n_2)^2} = W_{n_1,\,n_2}, \tag{16}$$

belong several elliptic orbits. Sommerfeld discusses these at some length [10, §§ 5, 6] in connection with the *intensity* question of the emitted lines. This interesting subject deserves some attention.

6. Notice that, by (2), p. 4, all the ellipses belonging to *the same* W have *equal major* axes, $2a = e^2/W$; and, remembering that the semi-minor axis is $b = \frac{p_1^2}{me^2}\cdot\frac{1}{\sqrt{1-\epsilon^2}}$, we have, by (16) and (14),

$$a = \frac{e^2}{2Nhc}(n_1+n_2)^2,^{*}\quad \frac{b}{a} = \frac{n_1}{n_1+n_2}. \tag{17}$$

The Balmer series of hydrogen is given by (15), when we put

$$n_1'+n_2' = \text{const.} = 2,$$
$$n_1+n_2 \ = 3,\ 4,\ 5,\ \ldots\ \infty.$$

The lines are emitted when the electron passes from one of the latter, initial, to one of the former, final, orbits. Both n_1 and n_2 are *positive* integers (such being the integrals $\int p_1 d\phi$, $\int p_2 dr$). As to *zero*, we can well have $n_2 = 0$, which, by (14), means $\epsilon = 0$, *i.e.* a *circular* orbit; but n_1 equal zero would mean $p_1 = 0$, *i.e.* a rectilinear orbit passing through the nucleus, and this cannot be treated (even approximately) without taking into account the relativistic terms,

* *i.e.*, with the value (8) for N, $\quad a = \frac{h^2}{4\pi^2 me^2}(n_1+n_2)^2$.

for the velocity would increase beyond limit. Therefore, in the present treatment, we have to assume

$$n_1 > 0, \quad n_2 \geqq 0. \tag{18}$$

Thus the final orbits ($n_1' + n_2' = 2$) are but *two* in number, viz.

$$\left.\begin{aligned} &n_2' = 0,\ n_1' = 2\ ; \quad \therefore\ b = a, \text{ by (17)}, \\ &n_2' = 1,\ n_1' = 1\ ; \quad \therefore\ b = \frac{a}{2}, \quad ,, \end{aligned}\right\}$$

The initial orbits are, always by (17) and (18),

$$\left.\begin{aligned} &\text{For } n_1 + n_2 = 3, \\ &\text{line } H_\alpha \text{ of} \\ &\text{spectrum series,} \end{aligned}\right\} 3 \text{ orbits, to wit } \frac{b}{a} = 1,\ \frac{2}{3},\ \frac{1}{3};$$

$$\left.\begin{aligned} &\text{for } n_1 + n_2 = 4, \\ &\text{line } H_\beta \end{aligned}\right\} 4 \text{ orbits, to wit } \frac{b}{a} = 1,\ \frac{3}{4},\ \frac{1}{2},\ \frac{1}{4},$$

and so on.

Thus the line H_α can be generated by a passage of the electron from three different initial to either of the two final orbits, *i.e.* in all in

$$2 \cdot 3 = 6 \text{ ways};$$

similarly, H_β in $\quad 2 \cdot 4 = 8$ ways;

H_γ in $\quad 2 \cdot 5 = 10$ ways,

and so on, in general, in $(n_1' + n_2')(n_1 + n_2)$ ways.

This number of possibilities, which thus far is only 'arithmetically' determined, Sommerfeld first reduces, on the ground of some quantist guesses ('quantentheoretische Vermutungen'), and then increases on the ground of some 'generalized assumptions,' in § 6 and § 7, respectively, of his paper [10]. These guesses are partly supported by spectroscopic experience. Of course, the quantists have still to seek, groping, their way through the marvellously complicated labyrinth of spectroscopic phenomena.

We have obviously, for every actual passage associated with radiation,

$$n_1 + n_2 > n_1' + n_2'.$$

Now, Sommerfeld assumes, in the way of a guess, that only *such passages are* '*possible*' for which, separately,

$$n_1 \geqslant n_1' \quad \text{and} \quad n_2 \geqslant n_2'. \tag{19}$$

These are Sommerfeld's '*Quantenungleichungen*,' which he attempts to bring into relation with *intensity* questions. These

considerations assume a more definite aspect when the hitherto single spectrum lines are resolved into several separate components; for, it will appear later that every one of the possible 'ways of generation' gives rise to a distinct line. This is due to the variability of the mass of the electron, and it will be better, therefore, to postpone details concerning this subject until we come to consider the relativistic complications. [The actual resolution becomes even more conspicuous through the agency of an electric field; Stark-effect. Cf. *infra.*]

Here it will be enough to state that Sommerfeld finds the rules (19), which instead of $n \cdot n'$ ways [I write $n_1+n_2=n$, $n_1'+n_2'=n'$] give only

$$n'(n-n'+1) \tag{19a}$$

ways of generation, in general well corroborated by the observations. Yet he adds that the first of (19) 'nur im *groben* richtig ist,' while the second alone, *i.e.*

$$n_2 \geq n_2', \tag{20}$$

is, 'under normal conditions,' satisfied without exception. The corresponding number of ways of generation is

$$n'\left(n-\frac{n'-1}{2}\right). \tag{20a}$$

As the measure of intensity of a line, due to the passage from an orbit n_1, n_2 to n_1', n_2', Sommerfeld proposes to consider, provisionally,

$$J=\frac{n_1'}{n_1'+n_2'}\cdot\frac{n_1}{n_1+n_2}. \tag{21}$$

inasmuch as none of the 'Quantenungleichungen' is violated; in the latter case the intensity is to be 'small' or zero.

The above rules reduce the arithmetically computed number of ways (nn'). On the other hand, an increase of this number is brought about by taking into account the orientation of the orbit in space. In fact, proceeding to quantize also the inclination α of the plane of the orbit with respect to an arbitrarily fixed reference plane, he finds that $\cos\alpha$ can assume only rational values, viz.

$$\cos\alpha=\frac{n_3}{n_2+n_3}, \tag{22}$$

where n_3 is a new integer, corresponding to $\int_0^{2\pi} p_\psi d\psi = n_3 h$, where ψ

is an angular coordinate (fixing, together with r and another angle, the position in space), and p_ψ the corresponding moment. But, in the absence of any physically given direction (say, an actually given axis of symmetry) such an ' orientation of the orbit plane in space ' is obviously meaningless. Sommerfeld is well aware of this fact, and he discusses this matter only in view of considerations concerning such phenomena as the Stark effect, in which the external (homogeneous) electric field offers an axis of reference. He mentions, in fact, in this connection Epstein's investigations on the Stark effect, without, however, entering deeply into them. We shall come to the quantum theory of the Stark effect, as worked out by Epstein and Bohr himself, a little later. Meanwhile let us go on with the review of Sommerfeld's own researches.

7. The most important and, at the same time, the most beautiful part of Sommerfeld's investigation is his explanation of the *fine-structure* of the hydrogen and similar series-lines by means of the *relativistic* treatment of the motion of the electron round the nucleus.

Sommerfeld does not omit to mention that the importance of the theory of relativity for the completion of his atom model was, on several occasions, pointed out by Bohr himself, who [4*a*] proposed also to view the hydrogen doublets as a relativistic effect, of the order of $\left(\frac{v}{c}\right)^2$.

But in taking up Bohr's suggestion, Sommerfeld modifies essentially the standpoint. While Bohr confined his attention to ellipses of evanescent eccentricity, Sommerfeld—in accordance with the first part of his investigations explained above—seeks the origin of the doublets and the more complicated ' lines ' in the *finitely* different, discrete values of eccentricity of his quantized elliptic orbits. [Cf. especially formula (14), p. 12, of the present report.]

To simplify matters Sommerfeld assumes the nucleus to be fixed [which, provided that m is ultimately replaced by $\frac{mM}{m+M}$, is sufficiently correct for the purpose in hand]. Then the force upon the electron is, also according to the theory of relativity,

rigorously given by e^2/r^2, and directed towards M, but the electron's mass is no longer constant; it becomes

$$m = m_0/\sqrt{1-\beta^2}, \quad \beta = \frac{v}{c},$$

and our previous equation of motion, (1), becomes

$$\frac{d}{dt}(m\dot{\mathbf{r}}) = -\frac{e^2}{r^2}\mathbf{u} \quad (\mathbf{r} = r\,.\,\mathbf{u}). \tag{23}$$

This gives a plane orbit, as before, and the integral of areas is again [we shall now write p instead of p_1]

$$p = mr^2\dot{\phi} = \text{const.}, \tag{24}$$

with the difference, however, that m is now a function of the velocity,

$$m = \frac{m_0}{\sqrt{1-\beta^2}}, \quad \beta = \frac{v}{c}, \tag{25}$$

m_0 being the so-called rest mass of the electron. The total energy E, which is another first integral, is easily found to be

$$E = -W = m_0c^2\left(\frac{1}{\sqrt{1-\beta^2}} - 1\right) - \frac{e^2}{r} = \text{const.} \tag{26}$$

[For a simple deduction of this from (23) see, for instance, my 'Theory of Relativity.']

The equation of the orbit is easily found to assume the form [with $\phi = 0$ as initial perihelion]

$$\frac{1}{r} = C(1 + \epsilon\,.\,\cos\gamma\phi), \tag{27}$$

where

$$\gamma^2 = 1 - \left(\frac{e^2}{pc}\right)^2, \quad C = \frac{e^2m_0}{\gamma^2p^2}\left(1 + \frac{E}{m_0c^2}\right), \tag{28}$$

and $\epsilon = \text{const.}$ If γ *differs but slightly from* 1, (27) represents an ellipse with slowly moving perihelion, to wit, the motion of the perihelion is *progressive* (as the astronomers say), *i.e.* in the sense of revolution, and amounts, angularly, per period of revolution, to

$$2\pi\left(\frac{1}{\gamma} - 1\right) \doteqdot \pi\left(\frac{e^2}{pc}\right)^2, \text{ by (28).} \tag{29}$$

Put $\frac{e^2}{c} = p_0$ [more generally, $p_0 = \frac{e}{c} \times$ charge of nucleus]; then

$$\gamma^2 = 1 - p_0^2/p^2. \tag{28a}$$

Thus for small $\frac{p_0}{p}$ the orbit is almost an ellipse with slowly moving perihelion. But when p approaches p_0, the orbit ceases to exhibit any resemblance to an ellipse and can, under certain circumstances, assume the form of a spiral. The manifestly all-important p_0, as defined above, will hereafter be referred to as the *critical* value of $p = mr^2\dot{\phi}$.

Using (24) and (26), and eliminating $\beta = v/c$, the energy belonging to a relativistic elliptic orbit will be seen to be

$$E = m_0c^2\left\{\sqrt{\frac{p^2 - p_0^2}{p^2 - \epsilon^2 p_0^2}} - 1\right\}. \tag{30}$$

The equation of the orbit, (27), (28), now becomes

$$\frac{1}{r} = \frac{m_0e^2}{\sqrt{(p^2 - p_0^2)(p^2 - \epsilon^2 p_0^2)}}\left\{1 \pm \epsilon\cos\left(\phi\sqrt{\frac{p^2 - p_0^2}{p^2}}\right)\right\}, \tag{31}$$

where the signs $\pm$ correspond to initial $\begin{matrix}\text{perihelion}\\ \text{aphelion}\end{matrix}$ taken as $\phi = 0$.

Notice that the quantized moment p is

$$p_n = \frac{nh}{2\pi},$$

and for $n = 1$,

$$p_1 = \frac{h}{2\pi},$$

so that the ratio of the critical or, as Sommerfeld calls it also, the 'universal' moment p_0 to p_1 is a small fraction, to wit,

$$\frac{p_0}{p_1} = \frac{2\pi e^2}{hc} \doteq 7 \cdot 10^{-3}, \tag{32}$$

for hydrogen (nucleus e), and for a nucleus of charge κe,

$$\frac{p_0}{p_1} \doteq \kappa \cdot 7 \cdot 10^{-3}.$$

If p approaches p_0 and, at the same time, $\epsilon \to 1$, we have, under some further specifications which need not detain us here, *spiral* orbits; but since in this case (velocity tending to c and therefore mass m growing without limit) the assumption of a fixed nucleus is illegitimate, Sommerfeld is not able to utilize these orbits for the spectrum theory. We can, therefore, omit here his short discussion of spiral orbits altogether, and confine ourselves to quasi-Keplerian ellipses.

Passing to the quantizing process, with respect to ϕ and r which continue to be *canonical* variables, we have, by (10), for the ϕ-coordinate,

$$p=\frac{n_1 h}{2\pi}, \tag{33}$$

while $\int p_r dr = n_2 h$ gives (since, owing to the motion of the perihelion we have now to integrate from

$$\phi=0 \text{ to } \phi=2\pi/\gamma\,;\ \gamma^2=1-p_0^2/p^2):$$

$$n_2 h=-p\int \frac{d}{d\phi}\left(\frac{1}{r}\right).dr=-p\int_0^{2\pi/\gamma}\frac{d}{d\phi}\left(\frac{1}{r}\right)\cdot\frac{dr}{d\phi}d\phi,$$

and this becomes, by (27),

$$\frac{1}{\sqrt{1-\epsilon^2}}-1=\frac{n_2 h}{2\pi\sqrt{p^2-p_0^2}}, \tag{34}$$

which quantizes again the eccentricity of the stationary orbits.

In virtue of (33) and (34) the expression (30) for the energy E, belonging to any stationary orbit, becomes, for a nucleus containing the charge κe,

$$1+\frac{1}{m_0 c^2}E=\left[1+\frac{(\alpha\kappa)^2}{\left[n_2+n_1\sqrt{1-\left(\frac{\alpha\kappa}{n_1}\right)^2}\right]^2}\right]^{-\frac{1}{2}}, \tag{35}$$

where α is the fraction (32), *i.e.*

$$\alpha\equiv\frac{2\pi e^2}{hc}\doteq 7\,.\,10^{-3}; \tag{36}$$

n_1, n_2 are independent positive integers, as before. Let us shortly denote the energy value following from (35) for a pair of integers n_1, n_2 by $E(n_1, n_2)$; then, if n_1, n_2 characterize the initial and n_1', n_2' the final orbit, the spectrum series corresponding to (35) will be, by Bohr's assumption (6), p. 6:

$$\frac{1}{\lambda}=\frac{1}{ch}\left\{E(n_1, n_2)-E(n_1', n_2')\right\}. \tag{37}$$

We see that, while according to Newtonian mechanics n_1 and n_2 entered only through their sum n_1+n_2 (giving a Balmer series of single lines), the integers n_1, n_2 enter into the relativistic energy (35) *separately*, so that the energies of the n_1+n_2 different orbits, corresponding to the same value of n_1+n_2, are no longer equal to one another. It is this which accounts for the complexity or fine-

structure of the spectrum lines, each 'line' now consisting of two or more separate components.

Since α^2, appearing in (35), is a small fraction, of the order $5 \cdot 10^{-5}$, Sommerfeld develops the energy expression into a power series of α^2. For the visible, and also the usual ultra-violet, region of the spectrum the series is needed only up to α^2. [The higher terms are of interest when the *Röntgen spectra* are aimed at, for we have then large κ; cf. *infra*.] Thus, rejecting α^4 and higher terms, (35) gives, with the previous meaning of N,

$$E = E_{(n_1, n_2)} = -\frac{Nhc \cdot \kappa^2}{(n_1+n_2)^2}\left\{1 + \frac{\alpha^2\kappa^2}{(n_1+n_2)^2}\left(\frac{1}{4}+\frac{n_2}{n_1}\right)\right\}. \qquad (38')$$

For hydrogen we have $\kappa = 1$; for helium, $\kappa = 2$, etc. The term independent of α, *i.e.* the factor of $\{\}$, is the previous, Newtonian value of E (corresponding to Newtonian mechanics); taken by itself, it would give the previous Balmer series; the α^2 term, due to relativistic complications (variability of mass), appears as responsible for the fine structure. To bring this into evidence, let us put $n_1+n_2=n$, and let us denote the said 'Newtonian' energy by E_n.* Then the last formula will become

$$E = E_{(n_1, n_2)} = E_n \cdot \left\{1 + \frac{\alpha^2\kappa^2}{n^2}\left(\frac{1}{4}+\frac{n_2}{n_1}\right)\right\}; \quad n = n_1+n_2. \qquad (38)$$

This, together with (37), shows us at a glance the modifications due to the relativistic variability of the electron's mass. There is, firstly, a general increase of E (and therefore of the corresponding frequencies) whose relative amount is

$$\frac{1}{4}\frac{\alpha^2\kappa^2}{n^2}. \qquad (A)$$

This Sommerfeld calls *the relativistic correction of energy for circular orbits* (since $n_2 = 0$ means: circular orbit, $\epsilon = 0$). Secondly, we have an increase of E of the several ellipses, whose relative amount is

$$\frac{n_2}{n_1}\cdot\frac{\alpha^2\kappa^2}{n^2}, \qquad (B)$$

which is thus seen to be *different* for different ellipses (all corresponding to the same $n = n_1+n_2$), and increasing with their eccentricity. To these *different* increases corresponds a *splitting* of

* *I.e.* let $$E_n = -\frac{Nhc\kappa^2}{n^2}.$$

the ' lines,' which now become groups of two and more components ; Sommerfeld calls, therefore, the relative energy increase (B) *the splitting of energy* (' Aufspaltung der Energie '). By what was said before, the approximate value of the pure number α^2, fundamental for these shifts and splittings, is $\alpha^2 \doteq 5 \cdot 10^{-5}$.

Sommerfeld, with a view to Röntgen spectra, proceeds to develop the energy up to α^6 inclusively ; but this matter need not detain us here.

What is here of importance is that the theoretical rules laid down in (A), (B) or in (38), with (37), have turned out to be admirably obeyed by the observed spectroscopic facts.

It would greatly exceed the limits of this report to quote all the detailed instances of the marvellous agreement between theory and experiment. We shall, therefore, confine ourselves to a few instances.

As an immediate consequence of the above formulae, the Rydberg factor in the Balmer series of hydrogen, instead of being equal, to N say, for all lines, should become

$$N' = N\left[1 + \frac{\alpha^2}{4}\left(\frac{1}{2^2} + \frac{1}{n^2}\right)\right], \tag{39}$$

where $n = 3, 4, 5$, etc., for the lines H_α, H_β, H_γ, etc. Now, Paschen's measurements of $\frac{\Delta N'}{N}$,* which were most exact and most reliable for $H_\alpha - H_\beta$, gave

$$10^6 \frac{\Delta N'}{N} = 0{\cdot}37,$$

while (39) gives, for $H_\alpha - H_\beta$,

$$10^6 \frac{\Delta N'}{N} = 0{\cdot}61,$$

which is certainly a satisfactory agreement, giving *the same order of magnitude*,—and hardly more than this could be expected in view of the difficulty of such refined observations and of the uncertainty of α^2,—and the *same sign of* $\Delta N'$. [*N.B.*—A certain theoretical modification due to Planck would give the wrong sign

* Paschen quotes (*Ann. Phys.* **50**, p. 935) for $H_\alpha H_\beta$ the ' corrected ' wave-lengths 6564·6592, 4862·7116 and, while he tries to represent the series by $N' \cdot \left(\frac{1}{2^2} - \frac{1}{n^2}\right)$ he finds $N'_{H_\alpha} = 109678{\cdot}205$, $N'_{H_\beta} = 109678{\cdot}164$. For details cf. Paschen, *l. cit.*

and the wrong order of magnitude, to wit, $-0{\cdot}48 \cdot 10^3$, instead of Sommerfeld's $+0{\cdot}61$; this speaks in favour of Sommerfeld's as against Planck's proposed 'Quantenansatz.' For details see [10], pp. 57-59.]

But much more remarkable are the many instances of agreement of theory and observation relating to the *fine-structure* (splitting) of the lines of hydrogen and of ionized helium, not only with regard to the configuration and distance between the components or satellites, but very often also with regard to their intensity. Again, in several cases, Paschen [in assiduous, reciprocal, communication with Sommerfeld] was able to discover a new component or satellite only after its existence was insistently predicted to him by his theoretical colleague.

Let us quote at least a few examples of such fine-structure agreement.

For $n = n_1 + n_2 = 2$ there are, as already mentioned, two possibilities, $2+0$ and $1+1$. Thus the constant term, $1/2^2$, of the Balmer series of *hydrogen* (corresponding to two final orbits) should give rise to a *doublet*,* whose components should show a *frequency difference*, which—to a first approximation—is equal to

$$\Delta\left(\frac{1}{\lambda}\right)_H = \frac{N\alpha^2}{2^4} \qquad (40)$$

(where $N = 1{\cdot}097 \cdot 10^5$, $\alpha^2 = 5{\cdot}3 \cdot 10^{-5}$), *i.e.* constant † for all lines (H_α, H_β, etc.) and amounting to

$$\Delta\left(\frac{1}{\lambda}\right) = 0{\cdot}36_3 \text{ cm.}^{-1} \qquad \text{(Theory)}$$

Now, the best observations on H_α, which are due to Fabry and Buisson, gave

$$\Delta\left(\frac{1}{\lambda}\right)_{H_\alpha} = 0{\cdot}30_7 \text{ cm.}^{-1} \qquad \text{(Obs.)}$$

(For H_γ, Michelson finds 0·42, but it is the last quoted value which is considered to be the most reliable.) The agreement is good. Moreover, Sommerfeld shows that if the distance is measured not from the chief line of the first component, but from the mid-point between I*a* and I*b* (cf. Sommerfeld's paper, Fig. 2)

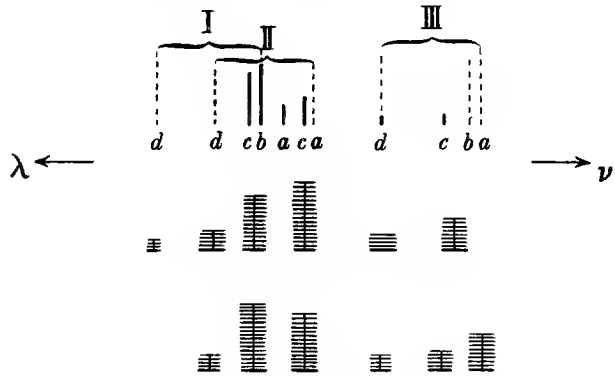
* Each component of these doublets will further consist of several subcomponents, owing to the multiplicity of the initial orbits.

† To a first approximation.

to the mid-point of II*b* and II*c* of the second component, Fabry and Buisson's value is increased by twenty-five per cent., thus giving $0{\cdot}38_2$ cm.$^{-1}$, which is still nearer the theoretical value $0{\cdot}36_3$.

Again, according to Sommerfeld's theory, [10], pp. 62-63, the *stronger* of the two components of the doublet should be the one on *the red side*, and such is also the observed fact.

Owing to the multiplicity of the initial orbits (variable term of Balmer series) each of the above components of the doublet should, according to the relativistically refined theory, consist of several distinct lines, and the intensity of these lines should *decrease* towards the red end of the spectrum (just the reverse of the components of the doublet, each taken as a whole). Each of the H_α components, for instance, should be a triplet, each of those of H_β and of H_γ a quartet and a quintet, respectively, and so on. Some of these fainter lines or 'satellites' are theoretically expected to be but very weak, some others should (in virtue of the 'Quantum-ungleichungen') be absent.

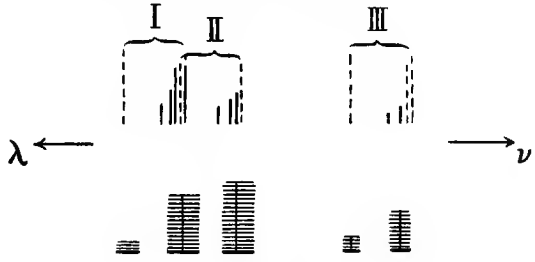


He 4686.

Now, many of these details, even those concerning the intensities, but more especially those concerning the multiplicity of a 'line' or, properly, group, and the relative distances between its components and satellites, are in most remarkable agreement with Paschen's careful spectroscopic observations, especially of helium.

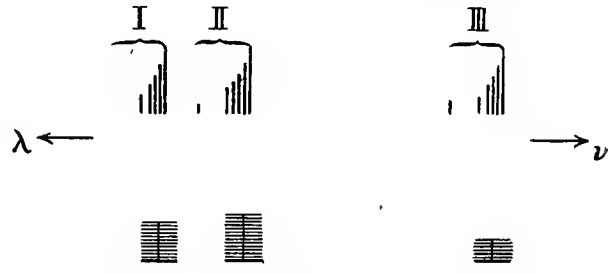
To see this, a glance at Sommerfeld's figures 4, 5, 6 (pp. 73, 75 [10]) will suffice. These three figures, which, with Sommerfeld's kind permission, are here reproduced, contain Sommerfeld's theo-

retical configurations of components with Paschen's observations juxtaposed.* The coincidence is striking.



He 3203.

Further, some slight defects in the constancy of the frequency difference between the components of the doublets are accounted for. According to Sommerfeld's theory this difference should tend



He 2733.

to constancy only for the higher members of the series, while in the first members there should be deviations from constancy,—which again seems to bring better harmony into the relation between the observational material and theory. This subject, intimately connected with the fine-structure of the components themselves, need not detain us any further. [For details, cf. [10], pp. 76 *et seq.*]

* The Roman numerals correspond to the *final* orbits as determined by $n_1' + n_2' = 3$, thus

3 + 0	I
2 + 1	II
1 + 2	III.

The last row in the diagram of He 4686 corresponds to a spark spectrum, the remaining shaded rows in all three diagrams correspond to the usual method of excitation.

Some of the observational material alluded to in the above lines and pages concerns hydrogen. But an important part of the verification of the theory was furnished by the observed spectra of *helium*, to which also the diagrams here given refer. Since the nucleus of the helium atom contains *twice* the charge ($2e$) belonging to the hydrogen nucleus, the frequency differences of the components of each line are, for helium, $2^4=16$ times greater than for hydrogen's analogous infra-red series. We have here in mind the principal series of helium, observed by Fowler, which—apart from the relativistic refinements—is represented by

$$\frac{1}{\lambda}=4N\left(\frac{1}{3^2}-\frac{1}{n^2}\right), \quad n=4,\ 5,\ 6,\ 7,\ \ldots, \tag{41}$$

and it will be enough to mention here some details concerning this series only. The constant term being $n_1+n_2=3$, each of the lines, coarsely represented by (41), should be a *triplet*, and the frequency differences between the 1st and 2nd, 2nd and 3rd component should bear to one another the ratio 1 : 3; to wit, if $\frac{N\alpha^2}{2^4}=0{\cdot}363$, mentioned previously, is shortly denoted by Δ_H, the said two frequency differences are, theoretically,

$$\Delta_1=\frac{128}{81}\cdot\Delta_H, \quad \Delta_2=\frac{128}{27}\cdot\Delta_H. \tag{42}$$

Now, Paschen's careful observations of the helium series (41), stimulated by Sommerfeld's predictions, have not only revealed, for the first time, the *triplet*-nature of each 'line,' but also the fine structure of each of the three components, especially for the first member of the series, $n=4$, but also for $n=5$, $n=6$. Several of the satellites, even the fainter ones, predicted by the theory, were detected, for the first time, on Paschen's spectrophotographic plates.

The Figures 4, 5, 6, of Sommerfeld, [10], given above concern precisely the 'lines' $n=4$, $n=5$, and $n=6$ of the series (41) with its relativistic correction and refinement terms.

The observations on helium, *ionized* helium that is,* provided, in fact, according to Sommerfeld's own opinion, the best confirmation of his theory, extending to almost all of its details. The

* For such is, according to general opinion, the 'helium' treated above; it has lost one of its electrons and, like hydrogen, retains but one.

details being all due to the relativistic refinement of Bohr's original theory, these experimental confirmations of the fine-structure constitute a new triumph of Einstein's 'old' theory of relativity (1905). It is well to bear this in mind, because of late many conservative physicists have thought that Relativity, after having accounted for Fresnel's dragging coefficient and for the variability of mass of the β-particles, had become barren.

The reader will have noticed that Sommerfeld's investigation is based on the Lorentz-Einstein electron, the mass of which is

$$m = m_0 (1 - \beta^2)^{-\frac{1}{2}}.$$

It may be interesting to note that K. Glitscher [11*a*], on W. Lenz's and Sommerfeld's suggestion, took up the question whether Abraham's rigid electron, for which the momentum is

$$mv = \frac{3}{4} m_0 \frac{c}{\beta} \left\{ \frac{1+\beta^2}{2\beta} \log \frac{1+\beta}{1-\beta} - 1 \right\}, \text{ instead of } mv = \frac{m_0 c \beta}{\sqrt{1-\beta^2}},$$

would show any observable differences with respect to the fine-structure of spectrum lines. With this purpose in view, Glitscher develops the general formulae, putting mv equal to any function of β, and applies them then to Abraham's electron, breaking off the series development of the energy with the α^2 term. The result is that, whereas Lorentz's electron, as in Sommerfeld's theory just reported, yielded $\alpha^2 = 5{\cdot}30 \cdot 10^{-5}$, harmonizing well with the best observed values $e = 4{\cdot}76 \cdot 10^{-10}$ and $h = 6{\cdot}51 \cdot 10^{-27}$, the rigid electron of Abraham would require at least $\alpha^2 = 6{\cdot}37 \cdot 10^{-5}$, while (according to Glitscher) e, h cannot be pushed beyond $4{\cdot}8 \cdot 10^{-10}$ and $6{\cdot}3 \cdot 10^{-27}$, giving only $5{\cdot}86 \cdot 10^{-5}$ for the spectroscopic constant α^2. In fine, Glitscher's pronouncement is decidedly against the rigid, and for the Lorentz electron. One cannot help pointing out a certain exaggeration and superfluity in this evidence. The superiority of the Lorentz electron was demonstrated some years ago by safer and more convincing methods, and there is no need to return to Abraham's electron.

We can omit here Sommerfeld's short discussion of the spectra of *neutral* helium (retaining both electrons) and of lithium, as well as his remarks on 'universal' spectroscopic units, such as his α used above, and shall pass on to give a short account of his investigations on the theory of Röntgen spectra, as laid down in [11]. This will occupy our attention in the next section.

8. *Röntgen spectra.* Let Z be the ordinal number of a chemical element in the periodic system (commonly denoted by N), and let κe be the charge of the nucleus of the atom of this element; put $l = Z - \kappa$. Then, according to Sommerfeld's theory, the 'lines' of the so-called K- and L-series should be *doublets* whose components are separated by a frequency distance

$$\Delta = (Z-l)^4 . \Delta_H,$$

where Δ_H is as in (40). Thus, the value of $\frac{\Delta}{(Z-l)^4}$ should be *constant*, and equal to $\Delta_H \doteq 0{\cdot}36$.

Now, this relation was excellently confirmed throughout the whole domain of the system of elements, from Cr to U (*i.e.* from $Z=24$ to $Z=92$), for which measurements were available (1916).* To give an idea of the closeness of agreement it will be enough to mention that

Cr Cu Zn Br Rh Ag (K-doublets)

gave, for $\Delta . (Z-l)^{-4}$, respectively,

0·43 0·40 0·39 0·47 0·35 0·44

and Ag Cs Pt Hg Th U (L-doublets)

whose Z are 47, 55, 78, 80, 90, 92, gave

0·39 0·39 $0{\cdot}44_5$ 0·45 0·49 0·50.

None of the values tabulated in Sommerfeld's paper—including many more than those given above—exceeds the limits 0·35 and 0·50.

It must be kept in mind that the deviations in the K-doublets are, perhaps, mainly due to the fact that their measured Δ's are uncertain to about 20 per cent. On the other hand, the L-doublets show a systematic rising of $\frac{\Delta}{(Z-l)^4}$ from 0·389, for $Z=47$, up to 0·498, for $Z=92$, which was to be expected on Sommerfeld's theory, the value $\Delta . (Z-l)^{-4} \doteq \Delta_H$ being only a first approximation. Sommerfeld's higher approximation is

$$\frac{\Delta}{(Z-l)^4} \doteq \Delta_H \cdot \left\{ 1 + \frac{5\alpha^2}{2} \frac{(Z-l)^2}{2^2} + \frac{53\alpha^4}{8} \frac{(Z-l)^4}{2^4} \right\}. \qquad (43)$$

* The value of l originally taken by Sommerfeld was 1. Later on he took $l=3{\cdot}5$, but even with $l=1$ the agreement is very good indeed. We may note that $l=1$ was adopted by Moseley.

But details of this kind need not detain us here any longer; nor can we enter, in a short report, into Sommerfeld's further investigation and discussion of the detailed structure of the Röntgen series of lines and their satellites, which is partly of a constructive and partly of a critical nature. Suffice it to say that even into this domain of phenomena Sommerfeld's work introduces order and clearness, which are likely to make the enormous observational material more ready for a thorough physico-mathematical treatment.

Leaving, therefore, the subject of the Röntgen spectra * and of the relativistic refinement of Bohr's theory, we will now pass to another topic, the effect upon spectrum emission of an external electric field, known as the Stark-effect, which offers yet another example of the conspicuous success of the quantum theory of spectra.

9. *Theory of the Stark-effect.* This was worked out by Sommerfeld's pupil, Dr. P. S. Epstein [7] and, independently of him, on somewhat different lines, by Schwarzschild, like Moseley and, alas, many others, prematurely lost to science and humanity in what is believed to be the 'last' war. Schwarzschild's paper (*Berl. Ber.* p. 548, 1916), the *last* work of this eminent physicist and mathematician,† being, unfortunately, inaccessible to me for the present, I shall base this part of the report on Epstein's paper alone, which, however, may be found sufficiently illuminating.

Epstein investigates an atomic system: nucleus of charge κe and a single electron-planet, as in section 2, but placed in an uniform electric field of intensity $\mathfrak{F}$. He disregards relativistic complications, so that his differential equation of motion is simply, with the x-axis along the electric field,

$$m\ddot{\mathbf{r}} = \nabla U, \quad U = -\frac{\kappa e^2}{r} - e\mathfrak{F}x; \quad r^2 = x^2 + y^2. \tag{44}$$

Mathematically this case is a sub-case of the famous problem of Euler-Jacobi (motion about two fixed centres), in which the

* Glitscher's investigation [11*a*], mentioned in Section 7, also condemns the unfortunate rigid electron in connection with the theory of the Röntgen spectra, inasmuch as it gives for the denominator of the first term of the *L*-series of doublets the value 1·892 instead of Sommerfeld's 2·000, which corresponds to a Lorentz-Einstein electron.

† Who died not 'in action,' but of an infectious illness contracted at 'the front.'

method of 'separation of variables' can be applied. In the present case the two variables ξ, η which have this property are those defined by

$$x = \tfrac{1}{2}(\xi^2 - \eta^2), \quad y = \xi\eta.$$

The third coordinate, ϕ, of the cylindrical system, with x as axis, has this property automatically. If p_ξ, p_η, p_ϕ be the corresponding moments, $p_\xi = \partial T/\partial\dot{\xi}$, etc., we have

$$p_\xi = \frac{m}{4}(\xi^2+\eta^2)\dot{\xi}, \quad p_\eta = idem.\ \dot{\eta}, \quad p_\phi = \frac{m}{4}\xi^2\eta^2\dot{\phi}.$$

Epstein adopts Sommerfeld's form of the quantizing-principle, and puts, therefore,

$$\int p_\xi\, d\xi = n_1 h, \quad \int p_\eta\, d\eta = n_2 h, \quad \int p_\phi\, d\phi = n_3 h, \tag{45}$$

n_1, n_2, n_3 being three independent integers. The last integral is simply taken between the limits 0 and 2π, as in the case of periodic orbits. The choice of the integration limits for ξ and η, however, requires some special care, since the orbits of the electron are, due to $\mathfrak{E}$, no longer periodic. Guided by the analogy of Sommerfeld's integrating over r (cf. *supra*) from $r_{\min.}$ to $r_{\max.}$ and backwards, Epstein decides to take the first of (45) twice between ξ_1 and ξ_2, and the second between η_1 and η_2, where ξ_1, ξ_2 and η_1, η_2 are those values for which $d\xi/d\eta = 0$, $d\eta/d\xi = 0$, respectively.*

With these limits the first two integrals (45) are evaluated approximately up to $\mathfrak{E}^2$, while the third integral offers no difficulty; the angular momentum, say $a\sqrt{m}$, round the x-axis being constant, the third of (45) or $\sqrt{m}\int_0^{2\pi} a\, d\phi = hn_3$ simply gives $a\sqrt{m} = hn_3/2\pi$.

The calculation of the $\mathfrak{E}^2$-terms of the first two integrals would offer some technical difficulties, but these higher terms are, for the present, scarcely needed, and Epstein, therefore, does not push his approximations beyond $\mathfrak{E}$. The expressions thus obtained

* $\frac{d\eta}{d\xi} = 0$ has also a third root η_3, but this is imaginary, and $\frac{d\xi}{d\eta} = 0$ has a third root ξ_3, which is real but $\left(\text{for } \mathfrak{E} \text{ small as compared with } \frac{\kappa e}{r^2}\right)$ enormous, while ξ_1, ξ_2 differ but little from their values for $\mathfrak{E} = 0$. These latter, therefore, are chosen for the purpose in hand.

contain, besides n_1, n_2, n_3, the energy constant W, and yield ultimately for the value of W for a stationary orbit characterized by n_1, n_2, n_3, the expression

$$W = \frac{\kappa^2 . Nch}{n^2} + \frac{3h^2 \mathfrak{E}}{8\pi^2 \kappa me} n(n_1 - n_2), \tag{46}$$

where $N = \frac{2\pi^2 me^4}{ch^3}$ is, as before, the Bohr value of the Rydberg constant, and

$$n = n_1 + n_2 + n_3.$$

The corresponding series of spectrum lines is, by Bohr's principle, (6), p. 6,

$$\frac{1}{\lambda} = \kappa^2 N \left[\frac{1}{n'^2} - \frac{1}{n^2} \right] + \frac{3h^2}{8\pi^2 \kappa me} \mathfrak{E} \{ n'(n_1' - n_2') - n(n_1 - n_2) \}. \tag{47}$$

The first term is the ordinary series of the Balmer type (for hydrogen $\kappa = 1$, etc.); the second term, proportional to the intensity $\mathfrak{E}$ of the electric field, gives *the Stark-effect, i.e.* a slight shift *and a splitting of the lines* given by the first term. For,

$$n = n_1 + n_2 + n_3$$

and $n' = n_1' + n_2' + n_3'$ being fixed, there are still, in general, several possibilities for the addends, and, therefore, for $n_1 - n_2$ and $n_1' - n_2'$ which appear in the second term.

Such then is Epstein's final formula of the Stark-effect, for hydrogenic [hydrogen-like] spectrum lines at least.

The resolution or splitting of lines is here somewhat similar to, but, with the electric fields available, much stronger than the relativistic one discovered by Sommerfeld. The comparison with observations is, therefore, in Epstein's case considerably easier. Paschen had to discover many of the components or satellites predicted by Sommerfeld, whereas owing to the assiduity of Johann Stark and his school, much good material was ready for comparison with the theory in question.

Now, the agreement of the theoretical effect, which for $\kappa = 1$ is, by (47),

$$\Delta\lambda^{-1} = \frac{3h^2}{8\pi^2 me} \mathfrak{E} . \Delta[n(n_1 - n_2)], \tag{47a}$$

with Stark's measurements on hydrogen lines, is even more striking than in the case of the relativistic refinement.

According to Stark's measurements the separation is *proportional* to $\mathfrak{E}$, as in (47*a*). [We will, however, not count this agreement as one of the triumphs of the theory; for the above series development was simply stopped at the $\mathfrak{E}$ term; it would rather seem incumbent upon Epstein to estimate the $\mathfrak{E}^2$-term and show that it is but a small fraction of the above 1st order term.] In the second place Stark's observations show that the separation is *symmetric* with respect to the original position of the line, and (47*a*) is in full agreement with this experimental result (interchanging n_1 with n_2, which does not change $n_1+n_2+n_3$, *i.e.* the original position, we have for every $+\Delta\lambda$ a corresponding $-\Delta\lambda$). But the most remarkable feature is the excellent *agreement of the several intervals* $\Delta\lambda$ between the electrically separated components, as obtained by Epstein's theory and by observation, to wit, in the case of the lines H_α, H_β, H_γ, H_δ of the Balmer series of hydrogen.

If, in (47*a*), we call n, etc., the integers of the constant term and m, etc., those of the variable term, the Balmer series will be given by

$$\begin{array}{c} n=2, \quad m=3, \quad 4, \quad 5, \quad 6, \ \ldots \\ (H_\alpha \ H_\beta \ H_\gamma \ H_\delta \ldots), \end{array}$$

and the last factor in (47*a*) will become

$$\Delta[n(n_1-n_2)] = m(m_1-m_2) - 2(n_1-n_2) = Z, \text{ say,} \qquad (48)$$

where $m=m_1+m_2+m_3$, $n_1+n_2+n_3=2$. Epstein adopts, as the basis of selection of possible Z-values, Sommerfeld's inequalities, extended also to the third integer n_3, *i.e.*

$$n_1 \leqslant m_1, \quad n_2 \leqslant m_2, \quad n_3 \leqslant m_3. \qquad (49)$$

He thus obtains, for the H line $(m=3)$, for instance, the following six possible values:

$$Z=5, \ 4, \ 3, \ 2, \ 1, \ 0; \qquad (H_\alpha)$$

similarly, for $m=4$, the seven values

$$Z=12, \ 10, \ 8, \ 6, \ 4, \ 2, \ 0, \qquad (H_\beta)$$

for $m=5$ (H_γ) as many as twenty different values, and for H_δ seventeen different Z-values.

Now, most of the theoretical components had been actually observed, and in all cases in which they were observed and their (wave-length) shifts measured, the results are in excellent agreement with the theory. Thus, for instance:

H_α

	$(Z=5)$	(4)	(3)	(2)	(1)	(0)	
$\Delta\lambda$ calculated:	14·7	11·7	8·8	5·9	2·9	0	Å. U.
,, measured:	—	11·5	8·8	6·2	2·6	0	

H_β

	(12)	(10)	(8)	(6)		(4)		(2)	(0)
calc.	19·4	16·1	12·9	9·7		6·5		3·2	0
meas.	19·4	16·3	13·2	10 & 9·7		6·7 & 6·6		3·3 & 3·4	0.
			p-comp.	s-comp.	p	s	p	s	

Here p and s stand for p-component and s-component, the usual notation of Johann Stark and others for light polarized *parallel, i.e.* with the electric oscillations parallel to the vector $\mathfrak{E}$, and *perpendicular* (s = senkrecht) to this vector.

Now, it is most remarkable that, as Epstein found without exception,

$$\left.\begin{array}{l} m_3 - n_3 \textit{ even} \text{ gives a } p\text{-component,} \\ \text{and} \quad m_3 - n_3 \textit{ odd} \text{ gives an } s\text{-component.} \end{array}\right\} \qquad (50)$$

This is also a good hint which Nature (observation) gives the groping quantist for the further development of his theory.

The above reproduction of the H_α- and H_β-tables does not exhibit this remarkable rule (50), but Epstein's full tables (*loc. cit.*, pp. 512, 513), show it in a striking manner. To quote but a few examples, we have for H_δ,

$Z=32$	28	24 $[m_3 - n_3$ even$]$
calc. $\Delta\lambda = 38{\cdot}1$	$33{\cdot}4$	$28{\cdot}6$,
obs. $\Delta\lambda = 37{\cdot}5p$	$33{\cdot}4p$	$28{\cdot}6p$,

etc., etc.

Even the intensities as based on theoretical guesses agree sufficiently well with the observations, especially if the last of (49) is replaced by $n_3 \leq m_3 + 1$, and under certain further clauses. But this aspect of the theory being still in its infancy, we may leave it for the present.

Epstein is certainly justified in concluding his elegant paper by the expression of the belief " that the communicated results offer a strikingly convincing proof for the '*Richtigkeit*' of Bohr's model of the atom."

The italicized word would stand for 'correctness.' But I am inclined to think that neither word is the proper one. I should prefer to say of such an atom model that it is a good working hypothesis, that—for the time being—it has a heuristic value,

and that it is not likely soon to exhaust itself as such. (Of course, it may become barren with time, as almost every theory hitherto constructed by man, but it promises to lead still to some further results agreeing with Nature.) Such, no doubt, was the meaning Dr. Epstein wished to convey by 'richtig.' He justly adds that, in the knowledge of atomic mechanisms—and thus far little more than hydrogen is covered—we are at the beginning of a new evolution, and that much still, it would seem, is to be expected from the quantum theory for the atomist.

Accordingly, the quantum theory of spectra should certainly become an attractive field for many investigators. It would seem also that it should stimulate a further refinement in the spectroscopic workshop, for—as can be seen from Paschen's and Sommerfeld's requirements—a further increase in resolving power and sharpness of images would help very much in testing the theoretical predictions and even in guiding quantists in elaborating and improving their theory.

10. The preceding sections describe the birth of the quantum theory of spectra and its definite and, as it seems, well consolidated progress practically up to the present time. Investigations other than those treated above have, thus far, more or less the character of attempts, in many cases promising, no doubt, but yet immature. Upon these it will perhaps be enough to touch briefly in this concluding section of our report.

The quantum theory of the effect upon spectrum emission of a *magnetic field* (*Zeeman phenomenon*) has been worked out by Sommerfeld, Debye, and Herzfeld, and, more recently, discussed on somewhat different lines by Bohr [15], Part II, and by H. A. Kramers [18]. It may be said that these interesting and elegant investigations account for the main features of the Zeeman effect as known from observation; but many important details are still to be dealt with,—and even some questions of a fundamental nature seem to remain unsettled. Moreover, as in the case of the problems previously mentioned, what has been worked out under this head is again the simplest atomic system representing hydrogen and hydrogen-like elements, whereas—especially with regard to the Zeeman effect—the theory of other, more complex, atomic systems would seem to be most desirable.

A promising attempt at an application of the quantum theory to the *photoelectric effect* and to the β-particles, emitted by radio-active substances was made by Epstein [8]. This is particularly interesting, from the theoretical standpoint, as—unlike the previous papers—it shows how to quantize the hyperbolic orbits appropriate to the escape of the electron. We may mention here that Epstein, while retaining Bohr's original principle, $h\nu = W' - W$, for the passage of the electron from one closed, *i.e.* elliptic, orbit to another such orbit, makes for the passage from an elliptic to a hyperbolic orbit the new assumption,

$$h\nu \geqq W_{\text{hyp}} - W_{\text{ell}} = h\nu_g, \tag{51}$$

where ν is the frequency of the light illuminating the atom and thus stimulating the passage in question, and ν_g is the limiting frequency, below which no 'photoelectric' electron is released. Epstein supports this assumption by some known experimental facts, as those found by Wagner and Kossel. The chief experimentally important result of Epstein's theory is the maximum velocity it yields. This latter agrees with observation very closely indeed, at least for Gehrcke and Janicki's experimental conditions (*Annalen der Physik*, xlvii, p. 679, 1915). With regard to the β-rays from radio-active substances, Epstein's calculated velocity of the electrons constituting these 'rays' shows a remarkable agreement with the measurements on radium *B* and *C* (Ra *B* and Ra *C*) made by Danysz, Rutherford and Robinson, and others. Yet, Epstein himself does not consider his theory in its present form as final, chiefly because he is not satisfied with his own arbitrary artifice by means of which he attempted to avoid the difficulty arising from the quantum-integrals becoming, in general, infinite for hyperbolic orbits. Notwithstanding this, his theory seems promising, especially with regard to the β-rays.

Turning to questions of a more general nature, we have to mention an interesting, although not unobjectionable paper by Th. Wereide [5] on the energy exchange 'between matter and aether.' Wereide attempts to reduce Planck's quantum hypothesis to things more plausible from the classical point of view. He gives also a very simple deduction of Planck's famous black body-radiation formula, and of the Balmer series, with Bohr's value

$2\pi^2me^4/h^3c$ of the Rydberg constant. Moreover, the former continuous spectrum appears only as a certain limiting case of line spectra or of what Wereide calls 'atomic radiation.' Unfortunately all these beautiful and stimulating results are obtained by furnishing the atomic system, and especially its nucleus, with an exact multiple of a certain magnetic quantum, the 'Kern-magneton.' Thus, it would seem, the whole difficulty associated with Planck's theory and concepts is only shifted back. Yet, Wereide's theory certainly deserves the attention of specialists.

A very important contribution to our subject, especially with a view to the hitherto neglected question of absorption, is made by Planck, 1917, in two most elegant and suggestive communications entitled *Zur Theorie des Rotationsspektrums* [16]. In opposition to Einstein's opinion (*Ber. deutsch. phys. Ges.*, 1916, p. 318), Planck assumes that Bohr's stationary orbits are not the only possible ones, but that they are the only orbits associated with *the emission* of radiant energy. This assumption has the advantage of being compatible with the laws of *absorption* deducible from classical electrodynamics, and Planck's purpose, in comparing the consequences of the said assumption with the experimental facts, in perfect harmony with the later form of his quantum theory,* is to save, if possible, these classical laws of absorption. Only if these consequences should turn out to disagree with the facts will it be necessary to abandon the classical theory also for absorption. With this purpose in view, Planck turns his attention to the absorption spectra—presumably due to the rotations of rigid electrical dipoles—investigated by N. Bjerrum, H. Rubens and others. In the first communication the axes of the dipoles are assumed to be fixed, in order to simplify the investigation in a first attempt. The second communication is devoted to an extension of the results to dipoles with free axes. Let N be the number of dipoles, each of electric moment E, per unit volume of the gas; of these let $NP(\varpi)\,d\varpi$ have their angular velocities contained between ϖ and $\varpi+d\varpi$. Then Planck's formula for the absorption coefficient α_{ϖ}, belonging to an incident radiation of frequency ϖ, can be written

$$\alpha_{\varpi}=-\frac{2\pi^2E^2N}{3cJ}\cdot\varpi^2\frac{d}{d\varpi}\left(\frac{P(\varpi)}{\varpi}\right), \tag{52}$$

* Concerning only the emission and not the absorption processes.

where J is the moment of inertia of each dipole. The most noteworthy feature of this value of the absorption coefficient is that α_ϖ vanishes not only for $P=0$, but, more generally, for any distribution-function P proportional to ϖ. Thus, if there is no absorption at all in a certain region of the spectrum, such as between two neighbouring absorption lines,

$$\varpi_n=\frac{nh}{2\pi J}, \quad \text{and} \quad \varpi_{n+1}=\frac{(n+1)h}{2\pi J}, \tag{53}$$

then, within this region, $P(\varpi)$ need by no means vanish, but must be *proportional* to the angular velocity ϖ itself. In fact, Planck finds also theoretically, by two different methods (a purely statistical, and an electro-dynamical one), that within every elementary domain of the phase-space P is equal to ϖ multiplied by a constant. He then proceeds to evaluate the jump of $P(\varpi)$ at the frontier $\varpi=\varpi_n$ of the $(n-1)^{\text{th}}$ and the n^{th} elementary domain, where ϖ_n is as in (53). This gives for the measure of the intensity of the absorption line at $\lambda=\lambda_n=4\pi^2cJ/nh$ an expression which, apart from a constant factor, is

$$\alpha_n=\frac{\psi^{n^2-n}(1-\psi^{2n})}{\sum_0^\infty (2n+1)\cdot\psi^{n^2+n}}, \tag{54}$$

where $\log\psi=-\frac{h^2}{8\pi^2JkT}$, h and k being the two familiar constants appearing in Planck's radiation formula, and T the absolute temperature. The coefficient α_n vanishes for $n=0$ as well as for $n=\infty$, and attains its maximum for $\psi^{2n}=(2n-1)(2n+1)$, *i.e.* for $n=\frac{2\pi}{h}\sqrt{JkT}$. Thus we should have maximum absorption at the wave-length

$$\lambda_{\max}=2\pi c\sqrt{\frac{J}{kT}}. \tag{55a}$$

Again, the intensity of a given absorption line λ_n, which varies with the temperature, will reach its maximum at the temperature

$$T_{\max}=\frac{\pi^2c^2J}{k\lambda_n^2}. \tag{55b}$$

These theoretical results are compared with the observations of Rubens and Hettner (*Berl. Ber.*, 1916, p. 179) on the rotation spectrum of water vapour, in an avowedly provisional way only,

since manifestly the H_2O-molecules cannot be regarded as simple dipoles. To the ordinal number $n=12$ of Bjerrum's series corresponds the absorption line $\lambda_n=14{\cdot}3\mu$, whence, by the relation $\lambda_n=4\pi^2cJ/nh$, the moment of inertia $J=9{\cdot}4\,.\,10^{-41}$, which is of the right order. The temperature of the vapour being $T=398$, this gives $\psi=0{\cdot}90$, and, by (55*a*),

$$\lambda_{max}=80\mu,$$

which would correspond to the absorption line $n=2$ of Bjerrum's series. This agrees well enough with Rubens and Hettner's experimental diagram, which shows a strong increase of absorption with decreasing value of n. Formula (55*b*) gives for the line $n=12$ a very high temperature for its maximum intensity, to wit, about 2800° C., which is much above the actual temperature (125° C.) at which the observations were made. But for the line $n=5$, *i.e.* $\lambda_n=33{\cdot}3\mu$, we should have only $T_{max}=580$, *i.e.* about 300° C. Thus, if the vapour were heated above 300°, this absorption line should be weakened. It seems that these predictions have not up to the present been tested experimentally. Reasons of space prevent us from dwelling any further upon this most attractive subject. We may add only that Planck himself is by no means satisfied with his own beautiful work.* Yet, it can scarcely be doubted that it will stimulate many new and important investigations both theoretical and experimental.

A few words must now be said about Bohr's own large memoir on *The Quantum Theory of Line Spectra* [15], which is to consist of four parts, but of which unfortunately only Parts I and II are yet published. A large portion of these two parts of this admirably written memoir is devoted to an account and to the discussion of work done by others since the publication (1913) of Bohr's first paper. Yet, especially in Part I, many new and promising general points of view are expounded, both with regard to the quantizing principles and concerning the probability of 'spontaneous transition' from a given stationary state to a

* In the concluding paragraph of his second communication [16] Planck considers a certain limiting condition [*loc. cit.*, p. 255, formula (51)] to be the weakest point in his chain of reasoning, while in a recent private letter to the present writer Prof. Planck says that what strikes him "unpleasantly ('unbehaglich') is that in his theory the frequency of the emitted and the absorbed light is identified with the frequency of rotation, which is in complete contradiction to Bohr's model."

neighbouring one. The latter subject is investigated in connection with the coefficients of the Fourier expansion of the displacement component of the mobile along any given direction. This subject of the *intensities* of spectral lines, which has since been developed further in a most masterly way by H. A. Kramers, reappears also in connection with attempts at finding criteria for the state of *polarization* of the emitted light under various external circumstances. A very valuable investigation on perturbed periodic systems is given in Part II, the purpose of which is to illustrate the General Theory laid down in Part I, using hydrogen as an example. The author happily advocates the use of the method of perturbations borrowed from celestial mechanics, and especially of what in the latter science is known as *the method of variation of elements*, secular variation, that is, of the elements of Keplerian motion. This facilitates the treatment of even such problems as that of the fine-structure of spectrum lines due to relativistic complications. The Fourier expansions are again taken up, in broad lines, and Kramers's paper, just quoted [18], is announced as an investigation in which it will be shown in detail how such calculations will enable us to account for the relative intensities of the fine-structure components, even as influenced by the experimental conditions of spectrum excitation,—a subject already pointed out by Sommerfeld in collaboration with Paschen. Both parts of Bohr's new memoir abound in hints which are likely to be very helpful in building up the theory of spectra originated by Bohr himself. Parts III and IV, in preparation, are to contain a discussion of problems arising in connection with 'spectra of other elements' (other, that is, than hydrogen), and a general discussion of the theory of the constitution of atoms and molecules on the lines of the quantum and the nucleus-atom theory.

A clear statement of the properties of so-called 'conditionally periodic' systems (an important concept in these investigations) in connection with the 'adiabatic invariants' of Ehrenfest [14], is given in a short paper [17] by J. M. Burgers, to which the reader must be referred for further information. Among more recent papers, not included in the list given at the beginning of the Report, we have to mention P. S. Epstein's new theoretical investigation of the Stark-effect in Fowler's helium series (*Ann. d. Physik*, lviii, pp. 553-576, April 1919), which proves his assumptions

for conditionally periodic motions and Bohr's theory of intensities to be in excellent agreement with Stark's measurements; further, a paper by Manne Siegbahn on 'Röntgenspektroskopische Präzisionsmessungen' (*ibid.*, lix, pp. 56-72, June 1919), giving further experimental support to Sommerfeld's theory, and a paper by W. Kossel and A. Sommerfeld (*Verh. deutsch. Phys. Ges.*, xxi, pp. 240-259, April 1919) entitled, 'Auswahlprinzip und Verschiebungssatz bei Serienspektren,' which, though not devoid of interest, seems thus far to be merely of an orientational and tentative character. It promises at any rate to open new roads to the still unexplored domain of non-hydrogenic spectra and to lay down some sure principles for their rational classification. The concept of atoms being built up of a number of electrons uniformly increasing throughout the periodical system plays a dominant rôle in Kossel and Sommerfeld's suggestive paper. The *selective principle*, used by these authors, and the associated *polarization rule* were deduced by A. Rubinowicz (*Phys. Zeitschr.*, xix, 1918) in a most remarkable way by the aid of the principle of conservation of electromagnetic momentum and moment of momentum. This subject is thoroughly expounded in the sixth chapter of Sommerfeld's admirable book on *Atomic Structure and Spectrum Lines* (Vieweg, Brunswick, pp. x+550, end of 1919). This masterly written work, which unfortunately reached me only after all the preceding pages of this Report were finally printed, may be warmly recommended to the care of the reader. Among a wealth of information on all related subjects, Sommerfeld gives also a good account of the chief investigations on the important question of *the ionization potential*, which for reasons of space could not be incorporated in the present booklet.

Whereas in all the investigations described in this Report the atomic nucleus is treated as a homogeneous sphere or, which is the same thing, as a point-charge, the present writer attempted in a recent paper [19] to work out the quantum theory of spectra emitted by atomic systems containing a 'complex,' *i.e.* any aspherical nucleus. The resulting series, whose members show a fine-structure altogether different from Sommerfeld's relativistic one, deviates also as a whole more or less from the Balmerian type according to the amount of asphericity of the nucleus. Applications of this theory, the chief results of which are condensed in

formulae (21)–(21·3) and (30)–(30·2), *loc. cit.*, are now in the course of preparation. A short account of the theoretical results was given at the Bournemouth meeting of the British Association (September, 1919).

The promised Parts III and IV of Bohr's own memoir [15], and, no doubt, many new papers due to other investigators will soon call for a supplement to the present Report which, owing to the rapid progress manifesting itself in this domain of research, will certainly be incomplete and much behind the times before it reaches the reader.

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